Copper Contamination in the Sediments of northern Kaohsiung Harbor, Taiwan

Chiu-Wen Chen, Chih-Feng Chen, Cheng-Di Dong

***Abstract*—**The distribution, enrichment, accumulation, and potential ecological risk of copper (Cu) in the surface sediments of northern Kaohsiung Harbor, Taiwan were investigated. Sediment samples from 12 locations of northern Kaohsiung Harbor were collected and characterized for Cu, aluminum, water content, organic matter, total nitrogen, total phosphorous, total grease and grain size. Results showed that the Cu concentrations varied from 6.9–244 mg/kg with an average of 109±66 mg/kg. The spatial distribution of Cu reveals that the Cu concentration is relatively high in the river mouth region, and gradually diminishes toward the harbor entrance region. This indicates that upstream industrial and municipal wastewater discharges along the river bank are major sources of Cu pollution. Results from the enrichment factor and geo-accumulation index analyses imply that the sediments collected from the river mouth can be characterized between moderate and moderately severe degree enrichment and between none to medium and moderate accumulation of Cu, respectively. However, results of potential ecological risk index indicate that the sediment has low ecological potential risk.

***Keywords*—**accumulation, ecological risk, enrichment, copper, sediment.

I. Introduction

COPPER (Cu) is a common environmental contaminant; It is an essential trace element for the growth of most aquatic organisms however it becomes toxic to aquatic organisms at levels as low as 10 μg/g [1]. Therefore, much research effort has been directed toward the distribution of Cu in water environment. Anthropogenic activities including mining, smelting, incinerator emissions, domestic and industrial wastewaters, steam electrical production, and sewage sludge are the major source of Cu pollution [1,2]. Cu has low solubility in aqueous solution; it is easily adsorbed on water-borne suspended particles. After a series of natural processes, the water-borne Cu finally accumulates in the sediment, and the quantity of Cu contained in the sediment reflect the degree of pollution for the water body [3].

Kaohsiung Harbor is located on the southwestern shore, and it is the largest international harbor in Taiwan. However, it receiving effluents from four contaminated rivers, including Love River, Canon River, Jen-Gen River, and Salt River. Results of recent research indicate that the Kaohsiung Harbor is heavily polluted with Cu, and the Love River and Canon River are both major pollution sources [4]. The two rivers flow through the downtown area of Kaohsiung City and finally discharged into Kaohsiung Harbor (Fig. 1). Love River and Canon River are located in Kaohsiung City's northern, basin area of about 45% of the entire Kaohsiung City, and regions along river have dense population with prosperous business and industrial establishments. The major pollution source includes domestic wastewater discharges, industrial wastewater discharges (e.g. paint and dye, chemical production, metal processing, electronic and foundry), municipal surface runoff, and transportation pollution [4]. All the pollutants will eventually be transported to the river mouth and/or harbor to deposit and accumulate in the bottom sediment.

The objective of this study is to investigate the Cu distribution in the surface sediment of northern Kaohsiung Harbor so that the degree of Cu enrichment, accumulation, and potential ecological risk can be evaluated.

II. Materials and Methods

Twelve sampling stations were distributed in northern Kaohsiung Harbor, Taiwan (Fig. 1). Sediment samples were collected at 12 stations selected in this study in February, 2011 with Ekman Dredge Grab aboard a fishing boat. After transported back to the laboratory, a small portion of the sample was subject to direct water content analysis (105^{o}C), and the remaining portion was preserved in -20^{o}C freezer to be analyzed later. Prior to being analyzed, each sample was lightly crushed with a wooden board, and then screened through 1 mm nylon net to remove particles with diameters larger than 1 mm. One portion of the screened portion was subject to particle size analyses using a Coulter LS Particle Size Analyzer [4,5]. Another portion was washed with ultra-pure water to remove sea salt; the salt-free particles were dried naturally in a dark place, grounded into fine powder with mortar and pestle made of agate, and then analyzed for organic matter (OM), total nitrogen (TN), total phosphorus (TP), total grease (TG), copper (Cu), and aluminum (Al). For Al and Cu analyses, 0.5 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids (HNO_3:HCl:HF=5:2:5), and was then heated to digest. The digested sample was filter through 0.45 μm filter paper; the filtrate was diluted with ultra-pure water to a pre-selected final volume. The Al and Cu content were determined using a flame atomic absorption spectrophotometry

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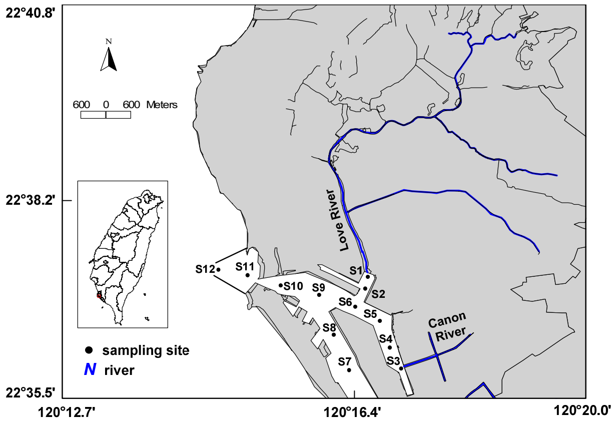

Fig. 1 Map of the study area and sampling locations

III. Results and Discussion

A. Sediment characteristics

It has been reported that the distribution of particle size, OM, TN, TP, and TG content were correlated to metal distribution in sediments [4]. Table 1 present the distribution of the major sediment characteristics in surface sediments at 12 monitoring stations studied. Results of sediment particle diameter analyses show that except Station S12, the major particles in sediment samples are silt (2–63 μm) with a range from 80.1% to 86.6%. Station S12, located at the harbor entrance, had the highest sand contents (92.9%) and the lowest silt contents (6.3%); whereas Stations 1 and 11 had the highest silt contents and the lowest sand contents (0.0–1.1%). Clay contents were in the range of 0.8–19.9%. Fine particles (dia. <63 μm) that can easily adsorb and accumulate pollutants are the major component of particles found in the studied sediment. The water content, OM, TN, TP, and TG in the sediments from the study area have a similar spatial evolution characterized by the highest levels at Stations 1–4, which are located at the vicinity of the mouths of Love River, and Canon River. TN, TP, and TG were relatively high in the vicinity of the mouths of river compared with those at the harbor entrance areas (Station 12). The results show that the anthropogenic contribution from the harbor tributaries is the major source of TN, TP, and TG.

B. Distribution of Cu in sediments

The contents of Al in the study sediments are between 4.18 and 5.29% with an average of 4.65±0.43% (Table 1). All surface sediment samples collected at 12 monitoring stations studied contain 6.9–244 mg/kg of Cu with an average of 109±66 mg/kg. Spatial distributions of Cu concentration in the surface sediment shown in Fig. 2 reveal that the sediment Cu content is relatively higher near the mouths of Love River, and Canon River (Stations 1–4), and gradually decreases in the direction toward the mouth of harbor (Station 12). These observations clearly indicate that the upstream pollutants brought over by rivers are the major source of harbor Cu pollution. The two rivers receive a great amount of industrial and domestic Cu from Kaohsiung city because about 44% domestic wastewater is discharged directly without adequate treatment. Moreover, several industrial plants (e.g. metal processing, paint and dye, chemical manufacturing, electronic, motor vehicle plating and finishing, and foundries) discharge industrial wastewater effluents into the tributaries in or adjacent to Kaohsiung city, and the pollutants are transported by river flow and finally accumulate near the river mouth. Some pollutants may drift with sea current to be dispersed into open sea [4,6].

Coefficient of the Pearson correlation between the sediment characteristics and Cu content is shown in Table 2. The surface sediment Cu content is obviously correlated to TG content ($p<0.01$) but not to either particle size ($p>0.05$) and OM ($p>0.05$) indicating that particle size and OM may not major factors to control the Cu distribution in this study areas. Although most studies presented significant negative correlation between sediment particle sizes, OM and Cu concentrations [4,7], results of this study indicated that TG contents were more important than grain size and OM in

TABLE I
Sediment Characteristics and Cu Contents in the Sediments of Northern Kaohsiung Harbor

Station	Clay (%)	Silt (%)	Sand (%)	Water content (%)	OM (%)	TN (mg/kg)	TP (mg/kg)	TG (mg/kg)	Al (%)	Cu (mg/kg)
S1	16.5	83.5	0.0	57.9	7.3	2665	655	1990	5.27	125
S2	17.8	82.2	0.0	113.2	6.0	2120	376	2284	5.29	244
S3	15.7	84.4	0.0	81.1	8.1	2762	736	1203	5.27	178
S4	13.6	86.2	0.2	93.0	6.6	2000	514	960	4.50	71.0
S5	14.5	84.9	0.6	86.7	3.7	1370	308	620	4.73	102
S6	18.0	82.0	0.0	91.2	4.9	1380	273	2440	4.40	121
S7	16.7	83.3	0.0	57.7	2.2	1089	213	410	4.40	76.0
S8	16.9	83.1	0.0	91.7	3.7	1103	261	1949	4.33	164
S9	14.3	85.2	0.5	86.1	4.0	1198	224	630	4.18	124
S10	13.9	84.9	1.1	42.1	2.8	1074	192	335	4.20	53.4
S11	19.9	80.1	0.0	58.9	3.9	1020	215	470	4.36	37.9
S12	0.8	6.3	92.9	28.6	3.4	875	294	305	4.84	6.9
Mean	14.9	77.2	7.9	74.0	4.7	1555	355	1133	4.65	109
SD	4.8	22.4	26.7	24.7	1.9	661	182	813	0.43	66

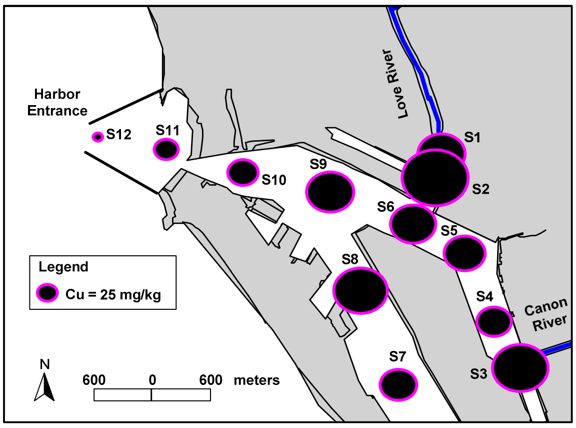

Fig. 2 Spatial distribution of Zn contents in surface sediment of northern Kaohsiung Harbor

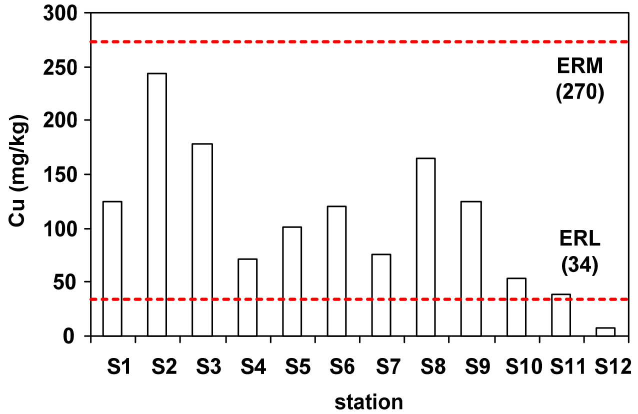

Fig. 3 Distribution of Zn contents in surface sediment of northern Kaohsiung Harbor

TABLE II
PEARSON CORRELATION COEFFICIENTS AMONG SEDIMENT CHARACTERISTICS AND CU CONTENTS (N = 12)

	Clay	Silt	Sand	Water content	OM	TN	TP	TG	Al
Silt	0.889[a]								
Sand	-0.924[a]	-0.997[a]							
Water content	0.545	0.581[b]	-0.583[b]						
OM	0.196	0.231	-0.228	0.407					
TN	0.154	0.210	-0.202	0.185	0.922[a]				
TP	0.048	0.203	-0.177	0.081	0.845[a]	0.882[a]			
TG	0.396	0.363	-0.374	0.720[a]	0.548	0.401	0.236		
Al	-0.078	-0.147	0.138	0.141	0.718[a]	0.802[a]	0.520	0.375	
Cu	0.499	0.480	-0.490	0.788[a]	0.517	0.465	0.147	0.776[a]	0.490

**Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed).

controlling the distribution of Cu in the sediments. The results might suggest that the sorption mechanism of Cu at the study areas sediments is mainly controlled by chemical adsorption, rather than physical or deposition of Cu with TG on surface sediments [4]. It is noted that the Cu distribution in sediments were significant positive correlation to TG contents (Table 2) which was usually derived from the upstream rivers with either industrial effluents or municipal sewage discharges.

C. Comparison with sediment quality guidelines

Several numerical sediment quality guidelines have been developed for assessing the contamination levels and the biological significance of chemical pollutants recently [8,9]. One of the widely used sediment toxicity screening guideline of the US National Oceanic and Atmospheric Administration provides two target values to estimate potential biological effects: effects range low (ERL) and effect range median (ERM) [8]. The guideline was developed by comparing various sediment toxicity responses of marine organisms or communities with observed metals concentrations in sediments. These two values delineate three concentration ranges for each particular chemical. When the concentration is below the ERL, it indicates that the biological effect is rare. If concentration equals to or greater than the ERL but below the ERM, it indicates that a biological effect would occur occasionally. Concentrations at or above the ERM indicate that a negative biological effect would frequently occur.

Fig. 3 shows the measured concentrations of Cu in comparison with the ERM and ERL values. Among the 12 sediment samples collected, the Cu is between ERL (34 mg/kg) and ERM (370 mg/kg) in 11 samples (91.7%), and only one sample collected from Station S12 is below ERL for Cu. This indicates that the concentration of Cu found in the study area sediments may cause adverse impact on aquatic lives. The study area is adjacent to the output of an industrial park that accommodates several chemical industrial plants using Cu compounds as raw materials. These plants are expected to release chemical pollutants which will accumulate in the bottom sediment of river mouth and harbor.

D. Enrichment factor

The enrichment factor (EF) is a useful tool for differentiating the man-made and natural sources of metal contamination [7,10]. This evaluating technique is carried out by normalizing the metal concentration based on geological characteristics of sediment. Aluminum is a major metallic element found in the earth crust; its concentration is somewhat high in sediments and is not affected by man-made factors. Thus, Al has been widely used for normalizing the metal concentration in sediments [4,7,11]. EF is defined as: $EF = (X/Al)_{sediment}/(X/Al)_{crust}$, where (X/Al) is the ratio of Cu to Al. The average Cu and Al content in the earth crust were 55 mg/kg and 8.23%, respectively, which excerpted from the data published by Taylor (1964) [12]. When the EF of a metal is greater than 1, the metal in the sediment originates from man-made activities, and vice versa. The EF value can be classified into 7 categories [13]: 1, no enrichment for EF < 1; 2, minor for 1 < EF < 3; 3, moderate for 3 ≤ EF < 5; 4, moderately severe for 5 ≤ EF < 10; 5, severe for 10 ≤ EF < 25; 6, very severe for 25 ≤ EF < 50; and 7, extremely severe for EF ≥50.

Table 3(a) show EF values of the sediment Cu for 12 monitoring stations studied; the Cu concentration is consistent with the Cu EF value for all sampling stations, and except station S12, all EF values are greater than 1. This indicates that the sediment Cu has enrichment phenomenon with respect to the earth crust and that all Cu originates from man-made sources. Stations S2 and S8 are classified as moderately sever enrichment, Stations S4, S7, and S10 are classified as minor enrichment, Stations S3, S3, S5, S6, S9 and S11 are classified as moderate enrichment, and Station S12 are classified as no enrichment, respectively. These results point out that the sediment near the mouth of rivers experiences severe enrichment of Cu that originates from the upstream sources of pollution. Additionally, the EF value of 5.05 obtained in Station S3 (Canon River mouth) is lower than the EF value of 6.7 reported earlier [4] indicating that the upstream pollution has been reduced so that the accumulation of pollutants in sediments is not as serious as during earlier years. This observation may show the effectiveness of intercepting the river flow and dredging the river mouth.

E. Geo-accumulation Index

Similar to metal enrichment factor, geo-accumulation (I_{geo}) index can be used as a reference to estimate the extent of metal accumulation. The I_{geo} values for the metals studied were calculated using the Muller's (1979) [14] expression: $I_{geo} = log_2 (C_n/1.5B_n)$, where C_n is the measured content of element Cu, and B_n is the background content of Cu 55 mg/kg in the average shale [12]. Factor 1.5 is the background matrix correction factor due to lithogenic effects. The I_{geo} value can be classified into 7 classes: 0, none for I_{geo} <0; 1, none to medium for I_{geo} = 0–1; 2, moderate for I_{geo} = 1–2; 3, moderately strong for I_{geo} = 2–3; 4, strong for I_{geo} = 3–4; 5, strong to very strong for I_{geo} = 4–5; and 6, very strong for I_{geo} >5.

Based on the I_{geo} data and Muller's (1979) [14] geo-accumulation indexes, the accumulation levels with respect to Cu at each station are ranked in Table 3(b). Stations S2–S3 are classified as moderately accumulation, Stations S1, S5, S6, S8, and S9 are classified as none to medium accumulation, and Stations S4, S7, and S10–S12 are classified as none accumulation.

F. Potential ecological risk

The potential ecological risk index (PERI) is applied to evaluate the potential risk associated with the accumulation of Cu in surface sediments. PERI that was proposed by Hakanson (1980) [15] can be used to evaluate the potential risk of one metal or combination of multiple metals. The PERI is defined as [15]: $PERI = PI \times T_i$, where *PI (pollution index)* $= (C_i/C_f)$; C_i is the measure concentration of Cu in sediment; C_f is the background concentration of Cu; T_i is its corresponding coefficient, i.e. 5 for Cu [16]. In this study, the average Cu concentration in earth crust of 55 mg/kg [11] was taken as the Cu background concentration. The calculated PERI values can be categorized into 5 classes of potential ecological risks [15,16]: low risk (PERI < 40), moderate risk (40 ≤ PERI < 80), higher risk (80 ≤ PERI < 160), high risk (160 ≤ PERI < 320), and serious risk (PERI ≥ 320).

TABLE III
EF, I_{GEO}, AND PERI OF CU FOR EACH STATION STUDIED AT NORTHERN KAOHSIUNG HARBOR

Station	(a) Enrichment factor			(b) Geo-accumulation index			(c) Potential ecological risk		
	EF value	EF class	EF level	I_{geo} value	I_{geo} class	I_{geo} level	PI	PERI	Risk level
S1	3.54	3	moderate	0.60	1	none to medium	2.3	11.4	low
S2	6.90	4	moderately severe	1.56	2	moderate	4.4	22.2	low
S3	5.05	3	moderate	1.11	2	moderate	3.2	16.2	low
S4	2.36	2	minor	-0.22	0	none	1.3	6.5	low
S5	3.22	3	moderate	0.30	1	none to medium	1.8	9.2	low
S6	4.11	3	moderate	0.55	1	none to medium	2.2	11.0	low
S7	2.63	2	minor	-0.12	0	none	1.4	6.9	low
S8	5.58	4	moderately severe	0.99	1	none to medium	3.0	14.9	low
S9	4.45	3	moderate	0.59	1	none to medium	2.3	11.3	low
S10	1.90	2	minor	-0.63	0	none	1.0	4.9	low
S11	1.30	2	moderate	-1.12	0	none	0.7	3.4	low
S12	0.21	1	no enrichment	-3.58	0	none	0.1	0.6	low
Mean	3.50	3	moderate	0.40	1	none to medium	2.0	9.9	low

[a] 1: EF <1 (no enrichment), 2: 1 < EF ≤ 3 (minor), 3: 3 < EF ≤ 5 (moderate), 4: 5 < EF ≤ 10 (moderately severe), 5: 10 < EF ≤ 25 (severe), 6: 25 < EF ≤ 50 (very severe), and 7: EF ≥50 (extremely severe) [13].

[b] 0: I_{geo} <0 (none), 1: I_{geo} = 0–1 (none to medium), 2: I_{geo} = 1–2 (moderate), 3: I_{geo} = 2–3 (moderate to strong), 4: I_{geo} = 3–4 (strong), 5: I_{geo} = 4–5 (strong to very strong), and 6: I_{geo} >5 (very strong) [14].

[c] PERI < 40 indicates low risk, 40 ≤ PERI < 80 is moderate risk, 80 ≤ PERI < 160 is higher risk, 160 ≤ PERI < 320 is high risk, and PERI ≥ 320 is serious risk [15].

Table 3(c) lists the PI value, PERI value, and risk classification for the Cu contained in the surface sediment samples collected in this study. All stations are classified as low risk with respect to Cu pollution. The above evaluation results indicate that the Cu contained in surface sediments at the study area has low potential ecological risks. However, the PERI value near the river mouth of Stations S2–3 is higher than other sites (Table 3(c)).

IV. CONLUSIONS

The surface sediment samples collected from the northern Kaohsiung Harbor contain 6.9–244 mg/kg of Cu with an average of 109±66 mg/kg. The distribution of Cu in surface sediments reveals that the Cu originates from the river upstream discharges of industrial and domestic wastewaters; it is transported along the river and finally deposited and accumulated near the river mouth. Base on the comparison with SQGs, the sediments Cu concentrations may cause acute biological damage. Results from the EF and I_{geo} analyses imply that the sediments collected from the river mouth can be characterized between moderate and moderately severe degree enrichment and between none to medium and moderate accumulation of Cu, respectively. Compared to the EF values reported earlier [4], the degree of Cu enrichment at the river mouths has been obviously reduced. Results of potential ecological risk evaluation show that the Cu contained in surface sediment at northern Kaohsiung Harbor has low potential ecological risks. The results can provide regulatory valuable information to be referenced for developing future strategies to renovate and manage river mouth and harbor.

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